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Annual Progress Summary Report

AN INVESTIGATION OF POTENTIAL
WATER-SOLUBLE CHEMILUMINESCENT
MATERIALS

BY:

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A new highly efficient class of chemiluminescent oxalic acid derivatives, N-trifluoromethyl sulfonyl oxamides, has been discovered. One member of this class, N,N'-bis(2,4,5-trichlorophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide, has given the highest chemiluminescence quantum yield (34%) reported for a chemiluminescent reaction in an organic solvent system. Modification of the structure of these oxamides has produced water-soluble derivatives but none were chemiluminescent in aqueous media.

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1. INTRODUCTION

The American Cyanamid Company has conducted research on chemiluminescence since 1961 [1], with the objective of exploiting the inherent capabilities of chemiluminescence through the discovery of practical marking and illumination systems. The practical potential of chemiluminescence is based on:

(1) A high theoretical light capacity of 173,000 lm hr l^{-1} equivalent to the light output of a 40-watt incandescent bulb burning continuously for 2 weeks. This high light capacity makes chemiluminescence especially suited for portable lighting applications and for other applications where the use of distributed power is inconvenient or impossible.

(2) Chemiluminescence is cold light. Since heat and flame are absent, chemiluminescent systems can be used where conventional hot lights would cause fire or explosion. Automobile and aircraft accidents, coal mines, repair of gas transmission lines are examples.

(3) Reliability through long shelf life. Conventional battery systems gradually lose energy even when in storage. Chemiluminescent systems, in principle, can have indefinite storage lifetimes.

Chemiluminescent reactions with the efficiency required for practical use were unknown at the beginning of Cyanamid's research program. Even the fundamental chemistry required for the discovery of new chemiluminescent reactions was unavailable.

Following initial feasibility studies[2], a detailed mechanism study was begun in 1963 under contract with the Office of Naval Research to obtain the basic knowledge required to design efficient chemiluminescent reactions. This effort was successful[3] and led to the discovery of practical chemical light formulations under subsequent contracts with the U.S. Naval Ordinance Laboratory[4,5]. As a consequence of these programs, the light output efficiency of chemical light was increased more than 1600 times[6]. Under a more recent contract with the U.S. Naval Weapons Center, the light output was increased an additional threefold[7]. Concurrent with the later contracts, Cyanamid conducted an independent applied research and development program which developed one of the efficient formulations, oxalic ester chemiluminescence, into a practical chemical light system which is in current commercial and governmental use for a wide variety of applications.

Subsequently, the feasibility of a water-based oxalate ester chemiluminescent system was established[8] under contract (No. NAS 5-22303) with NASA's Goddard Space Flight Center. In a recent contract with the Office of Naval Research, the mechanism of the chemiluminescent system was investigated and further insight into the effects of key reaction variables on the excitation processes was obtained[9,10].
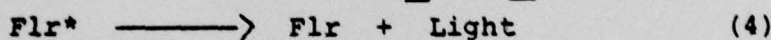
The current oxalic ester based system utilizes an organic solvent which constitutes most of its weight and volume. A substantial gain in light output per unit weight and volume could be achieved through development of a solid-state formulation comprised primarily of active ingredients. This formulation would be activated by contact with water at the point of use[11].

The objective of the present research effort is to produce a water-soluble oxalic ester derivative which when combined with the appropriate fluorescer and hydrogen peroxide will produce chemiluminescent emission efficiently. The initial phase of the program has concentrated on design and synthesis of efficient oxalic acid derivatives since these materials can be evaluated with currently available fluorescers. The optimum water-activated system will undoubtedly require new water-soluble fluorescers.

2. Chemiluminescence in Aqueous Media

A. Mechanism of Peroxyoxalate Chemiluminescence

Previous research[9,10] on the mechanism of peroxy-oxalate chemiluminescence indicates the following mechanism is in agreement with the available experimental data:

$$\overset{OO}{\overset{||\,||}{ROCCOR}} + H_2O_2 \longrightarrow \overset{OO}{\overset{||\,||}{ROCCOOH}} + ROH \qquad (1)$$

$$ROCCOOH \longrightarrow K.I. + ROH \qquad (2)$$

$$K.I. + Flr \longrightarrow [complex] \rightarrow Flr^* + 2CO_2 \qquad (3)$$

$$Flr^* \longrightarrow Flr + Light \qquad (4)$$
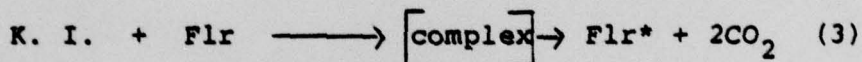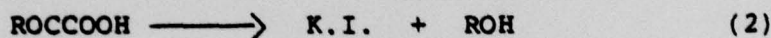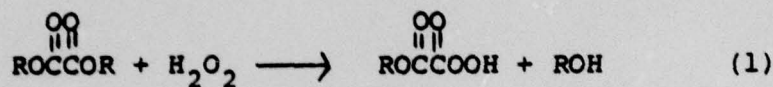
Steps (1) and (2) involve nucleophilic attack by hydrogen peroxide on the oxalic ester followed by unimolecular reaction of the peracid intermediate to generate the key chemiluminescent intermediate (K.I.), tentatively proposed to be 1,2-dioxetandione. The key intermediate then reacts with a fluorescent molecule to generate the first excited singlet state of the fluorescer (Flr*) while liberating two molecules of carbon dioxide. The excited fluorescer then emits light characteristic of a typical fluorescence process.

Steps (1) and (2) are base-catalyzed, but recent evidence[9] suggests these processes may involve general base catalysis rather than specific catalysis by the hydroperoxide anion. Further mechanistic studies are needed to clarify the details of the mechanism and to unequivocally establish the structure of the key intermediate.

B. Aqueous Reactions

Mechanistic studies carried out to date have concentrated primarily on peroxyoxalate chemiluminescent reactions in organic solvent systems. However, calculations based on the method of Ritchie[12], detailed in a recent proposal to the Office of Naval Research[11], indicate that efficient chemiluminescence in aqueous media should be feasible because of the higher nucleophilic reactivity of hydrogen peroxide compared to either water or hydroxide ion[13].

Since low concentrations of oxalic acid (ca. 10^{-4}M) have a pronounced quenching effect on the peroxyoxalate chemiluminescent reaction, design of optimum oxalic acid derivatives must maximize the selectivity of the hydrogen peroxide nucleophilic displacement over the hydrolysis reaction which not only consumes starting material but also produces oxalic acid or an oxalic acid derivative which would quench the chemiluminescent reaction.

The synthetic program was therefore directed towards the design and synthesis of new classes of oxalic acid derivatives in which the selectivity of the hydrogen peroxide reaction over the hydrolysis reaction would be maximized for optimum efficiency in an aqueous system.

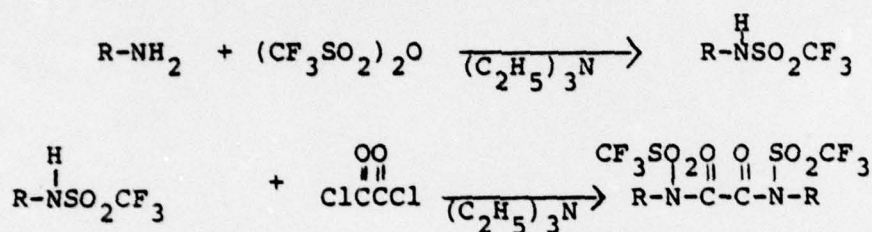3. Synthesis of New Chemiluminescent Materials

A. N-Trifyl Oxamides

One of the major obstacles in designing chemilum-
inescent oxalic acid derivatives for aqueous reactions
is the competitive hydrolysis to oxalic acid, a known
quencher of peroxyoxalate chemiluminescent reaction.
While oxamides are known in general to be hydrolytically
more stable than oxalic esters, the inherent organic
solvent chemiluminescence efficiencies of several sub-
stituted oxamides prepared in an earlier program were poor[2].
Since the efficiency of diaryl oxalic esters generally
increases with increasing substitution of electron
attracting groups on the aromatic nucleus, activation of
the oxamide nitrogen by substitution of strong electron-
attracting group, X, should enhance the effectiveness of

$$\underset{\displaystyle R-N-C-C-N-R}{\overset{\displaystyle X\quad O\quad O\quad X}{}}$$
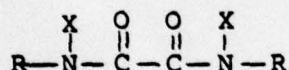
the leaving group and thereby improve chemiluminescence
efficiency. One of the strongest neutral electron with-
drawing groups known[14] is the trifluoromethyl (CF_3SO_2-) or
triflyl group. A series of N-triflyl oxamides was there-
fore prepared to determine whether sufficient activation
could be achieved from this group to permit trifyl oxamides
to serve as a basis for design of water-soluble analogs.

The general method for preparation of these oxamides is summarized in Scheme I shown below.

Scheme I

Synthesis of N-Trifyl Oxamides

$$R-NH_2 \ + \ (CF_3SO_2)_2O \ \xrightarrow[(C_2H_5)_3N]{} \ R-\overset{H}{N}SO_2CF_3$$

$$R-\overset{H}{\underset{|}{N}}SO_2CF_3 \ + \ Cl\overset{O\,O}{\underset{}{CCCl}} \ \xrightarrow[(C_2H_5)_3N]{} \ R-\overset{CF_3SO_2}{\underset{}{N}}-\overset{O}{\underset{}{C}}-\overset{O}{\underset{}{C}}-\overset{SO_2CF_3}{\underset{}{N}}-R$$
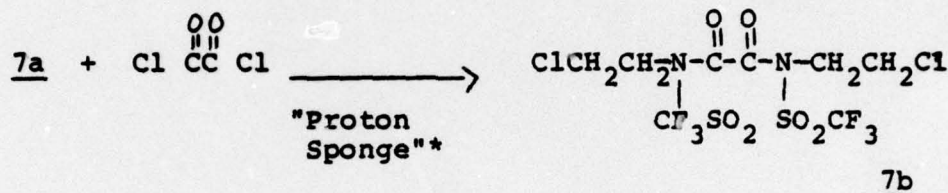
The appropriate primary amine is treated with triflic anhydride at low temperature following procedures similar to those described by Hendrickson and Bergenson.[15] The acidic triflamides are then acylated with oxalyl chloride in the presence of an amine acid acceptor yielding the desired triflyloxamide. Analytical data for the N-substituted triflamides and the related trifyl oxamides is summarized in Tables 1 and 2 respectively. Chemiluminescent performance of the oxamides is discussed in section 3 of this report.

The presence of a labile chlorine atom in the 2-chloroethyl trifluoromethylsulfonylamide (7a) necessitated a modification of the method described in Scheme I. The oxamide was prepared by the route summarized in Scheme 2.

Scheme 2

Synthesis of N,N'-Bis(2-chloroethyl)-N,N'-Bis
(trifluoromethylsulfonyl)oxamide (7b)

$$ClCH_2CH_2NH_2 \cdot HCl + CF_3SO_2Cl \xrightarrow[\text{Molecular Sieve}]{3A} ClCH_2CH_2\overset{H}{N}SO_2CF_3 + 2HCl$$

7a

$$7a + Cl\overset{O\ O}{\underset{}{CC}}Cl \xrightarrow[\text{Sponge"*}]{\text{"Proton}} ClCH_2CH_2\underset{CF_3SO_2}{N}-\overset{O}{C}-\overset{O}{C}-\underset{SO_2CF_3}{N}-CH_2CH_2Cl$$

7b
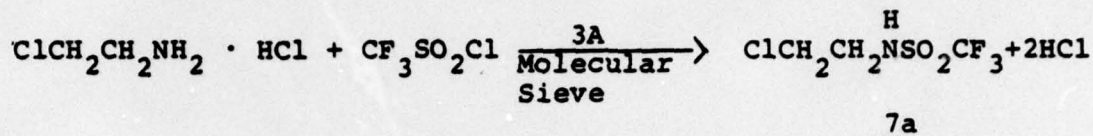
*"Proton Sponge"[R] is 1,8-bis-(dimethylamino)naphthalene
from Aldrich Chemical Company.

Use of powdered 3A Molecular Sieve[16] effectively
catalyzed the formation of the triflamide 7a and the use
of "Proton Sponge", a strong proton abstracting agent
which is a poor nucleophile[17] avoided displacement of the
chloride and afforded the oxamide in 80% crude yield.

The presence of the pyridyl nitrogen in 8a necessi-
tated a similar approach. The triflamide was prepared by
Molecular Sieve catalysis of the reaction of 2-chloro-3-
amino pyridine with triflic anhydride. The trifyl oxamide
8b was prepared by Molecular Sieve catalyzed reaction of
oxalyl chloride with the triflamide 8a.
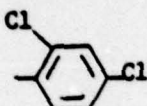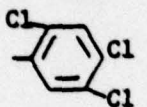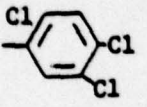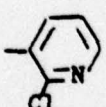
Several attempts to quaternize the pyridyl nitrogens

8b

8c
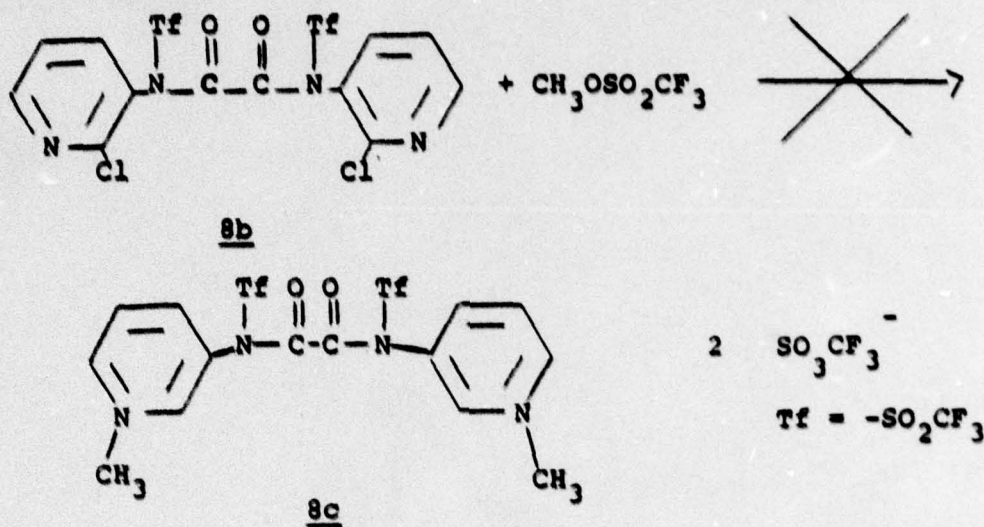
in **8b** with methyl triflate and thereby introduce water solubility were unsuccessful. Treatment of **8b** with methyl iodide gave only recovered starting material.

TABLE 1

N-SUBSTITUTED TRIFLAMIDES: $\overset{H}{R}NSO_2CF_3$

COMPOUND R =	Yield	mp		Elemental Analysis					
				C	H	N	S	F	Cl
1a. (4-Cl-phenyl)	93%	45-7	Calcd	32.43	1.93	5.41	12.36	22.01	13.51
			Found	32.49	1.80	5.55	12.21	21.79	13.30
2a (2,4-diCl-phenyl)	97%	84-6	Calcd	28.67	1.37	4.78	10.88	19.39	23.89
			Found	28.55	1.44	4.85	11.15	18.95	24.00
3a (2,4,5-triCl-phenyl)	82%*	104-6	Calcd	25.69	0.92	4.28	9.79	17.43	32.11
			Found	25.59	1.00	4.35	9.95	17.00	31.98
4a (2,4,5-triCl-phenyl)	91%*	99-101	Calcd	25.69	0.92	4.28	9.79	17.43	32.11
			Found	25.52	0.98	4.40	10.01	17.31	32.15
6a -CH₂CH₂OCH₃	99%	bp 50-1° at .5mm	Calcd	23.19	3.86	6.76	15.46	27.54	
			Found	22.94	3.73	6.49	15.15	26.95	
7a -CH₂CH₂Cl	31%*	bp 53-5° at .5mm	Calcd	17.06	2.37	6.64	15.17	27.01	16.59
			Found	17.42	2.51	6.54	15.38	26.79	16.21
8a (2-Cl-pyridyl)	48%*	120-2	Calcd	27.69	1.54	10.77	12.31	21.92	13.46
			Found	27.85	1.41	11.00	11.95	21.50	13.66

*CRUDE YIELD

TABLE 2

N-SUBSTITUTED TRIFYL OXAMIDES:

$$CF_3SO_2NCCNSO_2CF_3$$
$$\underset{R}{}\overset{O\ O}{\underset{R}{}}$$

| COMPOUND R =	mp		ELEMENTAL ANALYSIS					
			C	H	N	S	F	Cl
1b (–C₆H₄–Cl)	173-4	Calcd	33.50	1.40	4.88	11.17	19.90	12.40
		Found	33.51	1.38	4.74	11.52	19.61	12.10
2b (dichlorophenyl)	148-50	Calcd	29.92	0.90	4.36	10.00	17.75	22.12
		Found	30.24	1.02	4.24	10.45	17.19	22.27
3b (trichlorophenyl)	190-2	Calcd	27.02	0.57	3.94	9.02	16.04	29.91
		Found	27.02	0.63	3.84	8.90	16.64	30.06
4b (trichlorophenyl)	170-2	Calcd	27.02	0.57	3.94	9.02	16.04	29.91
		Found	26.91	0.60	3.80	8.85	16.40	30.02
5b (–C₆H₄–NO₂)	172-5	Calcd	34.16	1.42	9.96	11.39	20.28	
		Found	34.46	1.25	9.80	11.78	19.82	
6b –CH₂CH₂OCH₃	bp 74-6 .5 mm	Calcd	25.64	2.99	5.98	13.68	24.36	
		Found	25.60	3.11	5.77	13.92	23.95	
7b –CH₂CH₂Cl	71-3	Calcd	20.17	1.68	5.88	13.45	23.95	14.71
		Found	20.05	1.49	5.92	13.20	23.60	14.98
8b (chloropyridinyl)	104-6	Calcd	29.27	1.05	9.76	11.15	19.86	12.20
		Found	29.10	1.14	9.51	10.89	19.40	11.95

B. Other Oxalic Acid Derivatives

Earlier reports[2,18] have indicated that 2-pyridyl oxalic acid derivatives are moderately efficient chemiluminescent compounds in non-aqueous media. Mechanistic studies indicated that an acid-catalyzed rearrangement actually occurs prior to the chemiluminescent reaction, converting the initially formed amide to the pyridyl oxalate which then undergoes the usual hydrogen peroxide light-producing pathway.
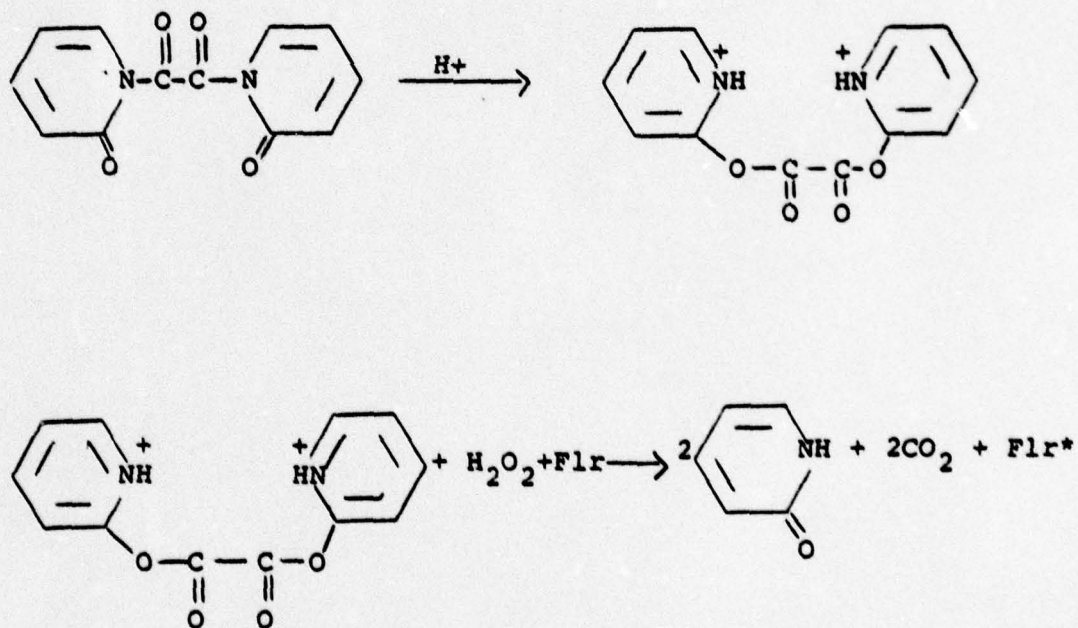
The rearrangement to the active oxalic ester would not be required in the ester of 3-hydroxypyridine and quaternization of the pyridyl nitrogens should introduce water solubility and reactivity comparable to the 2-pyridone series. Thus, bis(3-pyridyl) oxalate **9a** was prepared in the usual manner from 3-hydroxypyridene and oxalyl chloride. This compound, bis(3-pyridyl)oxalate **9a**, gave a bright but short-lived (ca. 5 seconds) chemiluminescent reaction in a non-aqueous (phthalate ester) solvent system. The presence of the basic pyridyl nitrogen could produce this type of effect. Quaternization of the pyridyl nitrogen with methyl triflate gave what appeared to be the desired oxalate ester, but the material was highly hygroscopic and attempts to obtain an analytically pure sample have thus far been unsuccessful.

Two derivatives of benzimidazole were converted to oxamides in the expectation that the imidazole nitrogen could be converted into a water soluble quaternary ammonium derivative.

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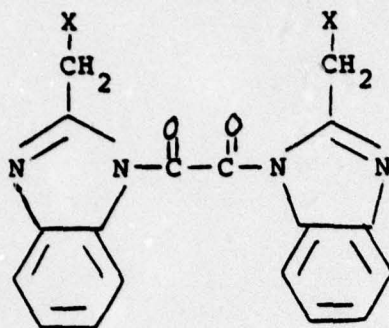
$\underline{10}$ x = Cl

$\underline{11a}$ x = H

Oxamide $\underline{10}$ was found to be unstable on standing at room temperature. The analogous methyl derivative was prepared and found to be unstable on standing at room temperature as was the corresponding quaternary ammonium compound $\underline{11b}$ prepared by treatment of $\underline{11a}$ with methyl triflate.

4. **Evaluation of New Chemiluminescent Materials**

N-trifyl oxamides substituted with electron with-
drawing groups have been found to produce the highest
chemiluminescence quantum yields ever reported for an
non-enzymatic reaction. Table 3 summarizes the perfor-
mance data for eight N-trifyl oxamides. Increasing
substitution of chlorine onto N-trifyl oxanilide causes
a concurrent increase in efficiency from 11% for the
4-chloro derivative (**1b**) to 26% (mean) for the 2,4-dichloro
compound (**2b**) to a high of 34% measured for the 2,4,5-
trichloro analog (**3b**). This efficiency is substantially
higher than the previous best efficiency of 23% reported[2b]
for bis-(2,4-dinitrophenyl)oxalate. The lower efficiency
of the 2,4,6-trichloro isomer (12.5%) was somewhat unexpected
in view of the higher performance of **2b** and **3b**. The 4-
nitro derivative was considerably more reactive than any
of the chlorinated oxanilides with a 3/4 lifetime of only
9 minutes.

The 2-methoxyethyl compound (**6b**), a liquid, gave
a quantum yield of about 3% and while some what miscible
with water, did not produce light emission on contact with
aqueous hydrogen peroxide. Infrared analysis of the
aqueous system (in an AgCl cell) revealed this oxamide
was hydrolytically stable under these conditions, suggesting
that insufficient activation by the methoxyethyl group was
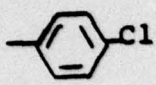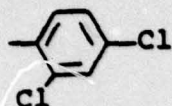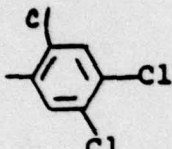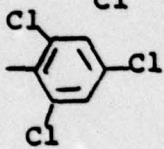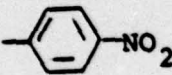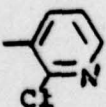responsible for the low efficiency in aqueous solution.

The high efficiency of the chlorinated trifyl
oxamides is very likely related to the ease of dis-
placement of the trifyl amide by hydrogen peroxide
in the chemiluminescent reaction the trifyl amides are
acidic (phenyl triflamide is reported to have a pKa = 4.4)[19]
and the conjugate bases would be expected to function as
good leaving groups in the nucleophilic displacement by
hydrogen peroxide. A steric effect might play a signifi-
cant role in lowering the efficiency of the 2,4,6-trichloro
compound (4b) compared to the 2,4,5-isomer (3b). This
steric effect would be in contrast to the results found
in the diphenyl oxalates where bulky ortho substitutents
generally increase chemiluminescence efficiency.

The very high efficiency found in the triflyl
oxamide series suggests that efficient aqueous chemilum-
inescence should be possible once the proper balance
between hydrolytic stability and chemiluminescent
reactivity is obtained. The triflyl oxamide series will
be examined further so a better understanding of structure-
activity can be obtained.

TABLE 3

CHEMILUMINESCENCE PERFORMANCE OF N-TRIFYL OXAMIDES[1]

$Tf\ N(R)COCO\ N(R)Tf$

COMPOUND R =	CONC M	Q.Y.[2] $x\ 10^{-2}$	Mean Q.Y.	T.75[3] min.	Light Capacity[4]
1b (4-Cl-phenyl)	.01	11.4		44.9	37.5
2b (2,4-diCl-phenyl)	.10	21.4		38.8	69.9
	.01	26.2		139	85.0
	.01	25.6	25.9	116	85.4
3b (3,4,5-triCl-phenyl)	.01	32.6		50.4	108
	.01	35.4	34.0	42.3	117
4b (2,4,6-triCl-phenyl)	.01	11.4		100	37.8
	.01	13.6	12.5	82.9	45.0
5b (4-NO_2-phenyl)	.01	11.0		8.88	35.7
6b $-CH_2CH_2OCH_3$	.10	2.85		70.2	9.20
7b $-CH_2CH_2Cl$	.01	3.68		125	12.2
8b (Cl-pyridyl)	.008	15.5		129	41.3

[1] Chemiluminescent reactions contained the indicated concentration of the oxamide, $6.75\times10^{-3}M$ 1-chloro-9,10-bis(phenylethynyl)anthracene, .375M hydrogen peroxide and $3\times10^{-4}M$ sodium salicylate in a solvent mixture of 75% (by volume) dibutylphthalate, 20% dimethyl phthalate, 5% t-butanol.

[2] Chemiluminescent quantum yield in Einsteins per mole of oxamide.

[3] Time required for 75% of the total light to be emitted.

[4] Integrated visible light output in lumen-hours per liter.

5. Experimental

Melting points were taken on a "Mel-Temp" block and are uncorrected. IR spectra were recorded on a Perkin-Elmer 297 spectrophotometer; samples were run in Nujol or in methylene chloride solutions. NMR spectra were recorded on a Varian Associates Model EM 360A spectrometer using tetramethylsilane as an internal standard. Mass spectra were recorded on a VG Micromass Model 7070 F high resolution mass spectrometer attached to a VG Model 2035 data system, using electron impact (EI) mode or chemical ionization (CI) mode. In the CI mode, methane was used as the reagent gas. Microanalyses were performed by the Micro Analytical Laboratories of American Cyanamid Company, Bound Brook, N.J. Microanalytical data is summarized in Tables 1 and 2.

Spectra and quantum yields for both fluorescence and chemiluminescence were obtained according to procedures previously described using the spectro-radiometer-lumino-meter developed by Roberts and Hirt[20]. The instrument was modified by using a RCA C31034 photomultiplier which gave satisfactory response over 350-700 nm range. The photo-multiplier and microchromater were calibrated against an NBS standard tangsten lamp using the reported fluorescence quantum yield of quinine sulfate[21]. The spectra thus obtained are corrected.

4-Chlorophenyl-trifluorophenylsulfonyl-amide (1a)

To a solution of 4-chloroaniline (5.12g, 0.04 mole) and triethylamine (4.04 g, 0.04 mole) in 60 mL of methylene chloride was added in portions 6.73 mL (0.04 mole) of trifluoromethanesulfonic anhydride at 0^oC under a nitrogen atmosphere. The mixture was stirred at room temperature for 4 hours. Evaporation of the solvent gave 10.2g of light brown oil, which solidified upon standing at room temperature. Recrystallization of the solid from cyclohexane gave 9.6g (93%) of pure 1a: IR (CH_2Cl_2) 3300, 1360, 1200 and 1140 cm^{-1}; NMR ($COCl_3$) δ 7.2 (s, 1 NH) and 7.3 to 7.4 ppm (25, aromatic protons); mass spectrum (EI), m/e 259 (M^+).

N,N-bis(4-chlorophenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide (1b)

Oxalyl chloride (0.5 me; 0.056 mole) was added dropwise to a stirred solution of 1a (2.6g; 0.01 mole) and triethylamine (1.0g; 0.01 mole) in 20 mL of 1,2-dimethyoxyethane at 0^oC under a nitrogen atmosphere. The mixture was stirred at 0^oC for 2 hours, heated to 60^oC, held at 60^oC for one hour, and evaporated to obtain a yellow solid which was treated with 20 mL of water. The solid remained after the water extraction was collected and recrystallized from anhydrous ether to give 2.46g (85%) of white crystalline 1b : IR (Nujol) 1750, 1730, 1210 and 1140 cm^{-1}; NMR ($COCl_3$) δ 7.30 to 7.65 ppm (m, aromatic protons); mass spectrum (EI), m/e 572 (M^+).

2,4-Dichlorophenyl-trifluoromethylsulfonyl-amide (2a)

To a solution of 2,4-dichloroaniline (5.0g, 0.03 mole) and triethylamine (3.1 g, 0.03 mole) in methylene chloride (50 mL) was added dropwise 5.2 ml (0.03 mole) of trifluoro-methanesulfonic anhydride at 0°C under a nitrogen atmosphere. After two hours of stirring of the reaction mixture, the solvent was evaporated to give a dark brown semisolid which was extracted into about 70 mL of anhydrous ether. Ether solution was dried over sodium sulfate. Evaporation of ether then gave 8.8 g (97%) of crude product which, after recrystalli-zation from methylcyclohexane, gave pure 2a: IR (Nujol) 3250, 1360, 1200 and 1140 cm^{-1}; NMR $(CDCl_3)\delta$ 7.20 (s,NH) and 7.30 to 7.70 ppm (m, aromatic protons); mass spectrum (EI), m/e 293 (M^{+}).

N,N'-Bis(2,4-dichlorophenyl)-N,N'-Bis(trifluoromethylsulfonyl) oxamide (2b)

To a solution of 2a (5.94 g; 0.02 mole) and triethylamine (2.0 g, 0.02 mole) in 50 ml of 1,2-dimethoxyethane was added dropwise oxalyl chloride (1.5 mL, 0.015 mole) at 0°C under a nitrogen atmosphere. After the addition was completed, the mixture was heated at 70°C for 5 hours. Triethylamine hydro-chloride precipitated from the solution and was filtered. Evaporation of the filtrate gave 6.05 g (94%) of crude product.

It was recrystallized from cyclohexane: IR(CH_2Cl_2) 1750, 1730, 1210 and 1130 cm^{-1}; NMR (acetone-d_6) δ 7.7 and 7.9 ppm (2 s. aromatic protons); mass spectrum (EI), m/e 642 (M^+).

2,4,5-Trichlorophenyl-trifluoromethylsulfonyl-amide (3a)

To a solution of 2,4,5-trichloroaniline (9.8 g; 0.05 mole) in methylene chloride (50 mL) was added in portions trifluoromethanesulfonic anhydride (8.4 ml, 0.05 mole) at 0^oC under a nitrogen atmosphere. The mixture was stirred at 0^oC for one hour, then was heated to 50^oC and stirred for 5 hours. The white solid precipitated was separated by filtration and the filtrate was evaporated to obtain a dark oil. Water was added to the oil and the resulting mixture was extracted three times with ether (150 mL). The combined ethereal extracts were then dried over sodium sulfate. Evaporation of the ethereal solution gave 13.4 g (82%) of crude product which, after recrystallization from cyclohexane, gave pure 3a: IR (CH_2Cl_2) 3300, 1260, 1210, and 1140 cm^{-1}, NMR ($CDCl_3$) δ 6.4 (s, 1NH), 7.6 and 7.8 ppm (2 s aromatic protons); mass spectrum (EI), m/e 327 (M^+).

N,N'-Bis(2,4,5-trichlorophenyl)-N,N'-Bis(trifluoro-methylsulfonyl) oxamide (3b)

Oxalyl chloride (1 mL, 0.01 mole) was added dropwise into a stirred solution of 3a (6.2 g; 0.02 mole) and tri-ethyl amine (2.0 g, 0.002 mole) in methylene chloride (50 mL) at $0^{\circ}C$ under a nitrogen atmosphere. After the addition was completed, the reaction mixture was stirred at room tempera-ture for 4 hours and then filtered to obtain 2.1 g of crude product. Recrystallization of the crude product from methyl cyclohexane gave the desired product **3b**: IR (CH_2Cl_2) 1750, 1730, 1340, 1210 and 1120 cm^{-1}; NMR (acetone-d_6) δ 7.7 and 7.9 ppm (2s aromatic protons); mass spectrum (EI), m/e 708 (M^+).

Evaporation of the filtrate, obtained by isolating the crude product and triturating the residue with water, gave an additional 3.5 g of crude product after filtering and drying. The total yield in two crops was 78.7%.

2,4,6-Trichlorophenyl-trifluoromethylsulfonyl-amide (4a)

To a solution of 2,4,6-trichloroaniline (4.91 g; 0.025 mole) and triethylamine (2.5 g; 0.025 mole) in methylene chloride (50 mL) was added dropwise 4.2 mL (0.025 mole) of trifluoromethanesulfonic anhydride at $0^{\circ}C$ under a nitrogen atmosphere. After the addition was completed, the mixture was stirred at room temperature for 3 hours. Evaporation of the reaction mixture obtained light brown semisolid; which was treated with water (40 mL) and then extracted three times with ether (150 mL). Ether layer then separated and was dried over sodium sulfate.

Evaporation of ether gave 7.43 g (91%) of crude product which was sublimed to obtain pure 4a; IR(CH$_2$Cl$_2$), 3300, 1260, 1210 and 1160 cm^{-1}; NMR (CDCl$_3$) δ 6.5 (S, 1NH) and 7.8 ppm (s, 2H, aromatic proton); mass spectrum (EI), m/e 327 (M$^+$).

N,N-Bis(2,4,6-trichlor henyl)-N,N'-Bis(trifluoromethyl sulfonyl) oxamide 4b)

Oxalyl chloride (2.0 mL, 0.02 mole) was added dropwise into a solution of 4a (8.0 g, 0.025 mole) and triethylamine (2.5g, 0.025 mole) in 1,2-dimethoxyethane (100 mL) at 0°C under a nitrogen atmosphere. After the addition was completed, the mixture was heated to 70°C for 15 hours. Triethylamine hydrochloride precipitated in the reaction mixture was filtered, and the filtrate was evaporated to give 6.5 g (73%) of crude product. It was recrystallized from cyclohexane: IR(CH$_2$Cl$_2$) 1740, 1380, 1260, 1210 and 1140 cm^{-1}; NMR (CDCl$_3$) δ 7.8 ppm (s 4H aromatic protons); mass spectrum (EI), m/e 708 (M$^+$).

4-Nitrophenyl-trifluoromethylsulfonyl-amide (5a)

To a solution of 4-nitroaniline (3.45 g; 0.025 mole) and triethylamine (2.5g; 0.025 mole) in methylene chloride (100 mL) was added in portions 4.2 mL (0.025 mole) of trifluoromethanesulfonic anhydride at 0°C under a nitrogen atmosphere, After the addition was completed, the mixture was allowed to warm to room temperature and stirred for another 2 hours. Evaporation of the solvent in reaction mixture gave 7.61 g of residual solid. To this solid was added 20 mL of water and then extracted with ether.

Ether layer that separated was dried over sodium sulfate.
Evaporation of ether gave 4.83 g (72%) of crude product;
IR (CH_2Cl_2) 3250, 1350, 1220 and 1140 cm^{-1}; NMR ($CDCl_3$) $\int$ 7.3
(s 1 NH) and 7.4 to 7.5 ppm (2s, aromatic protons); mass
spectrum (EI), m/e 270 (M^+).

N,N'-Bis(4-nitrophenyl)-N,N'-Bis(trifluoromethylsulfonyl) oxamide (5b)

Oxalyl chloride (0.65 ml, 0.0065 mole) was added
dropwise to a stirred solution of 5a (3.61 g; 0.013 mole)
and triethylamine (1.3 g 0.0013 mole) in dry tetrahydrofuran
(40 mL) at 0°C under a nitrogen atmosphere. After the
addition was completed, the reaction mixture was warmed to
room temperature and stirred for 18 hours. The reaction
mixture was then filtered, the filtrate was evaporated, and
water (20 mL) was added to the residue. The resulting pre-
cipitate was then filtered to obtain 3.29 g (92%) of crude
product. It was recrystallized from diethyl ether: IR
(CH_2Cl_2) 1750, 1730, 1350, 1210 and 1130 cm^{-1}; NMR ($CDCl_3$)
$\int$ 7.7 to 7.9 ppm (4s, aromatic protons) mass spectrum (EI),
m/e 562 (M^+).

2-Methoxyethyl-trifluoromethylsulfonyl-amide (6a)

To a solution of 2-methoxyethyl amine (3.75 g; 0.05
mole) and triethylamine (5.0 g, 0.05 mole) in methylene
chloride (40 mL) was added in portions 8.4 mL (0.05 mole)
of trifluoromethane sulfonic anhydride at $-78^{o}C$ under a
nitrogen atmosphere. After the addition was completed,
the mixture was stirred at $-78^{o}C$ for 2 hours, and then
evaporated. The residue thus obtained was extracted with
diethyl ether and the ethereal solution dried over sodium sulfate.
Evaporation gave 9.92 g (96%) of crude liquid product.
Vacuum distillation gave 7.85 g of pure 6a: IR (Neat)
3300, 3150, 1370, 1250, 1170 and 1120 cm^{-1}; NMR $(CDCl_3)$
δ 3.5^{o} (s 3H), 3.70 (s 4H) and 6.1 ppm (s 1NH); mass
spectrum (CI), m/e 208 $(M^{+}+H)$.

N,N'-Bis(2-Methoxyethyl)-N'N'-Bis(trifluoromethyl sulfonyl) oxamides (6b)

Oxalyl chloride (1 mL, 0.01 mole) was added portionwise
into a stirred solution of 6a (4.0 g; 0.02 mole) and tri-
ethyl amine (2.0 g; 0.02 mole) in 1,2-dimethoxyethane (40 mL0
at $0^{0}C$ under a nitrogen atmosphere. After the addition was
completed, the reaction mixture was stirred at $0^{0}C$ for one
hour, heated to $50^{o}C$ and stirred thereat for 2 hours, and
concentrated to remove the solvent. The residue was then
extracted with ether and then dried over sodium sulfate.
Evaporation of ethereal solution obtained 4.65 g(99%) of
crude product. Vacuum distillation of the crude product
gave pure 6b: IR (Neat) 1740, 1720, 1420, 1320, 1200, 1160

and 1120 cm^{-1}; NMR (CDCl$_3$) δ 3.40 (s, 3H), 3.70 (t, 2H, J= 6 Hz)and 4.00 ppm (t, 2H, J=6Hz); mass spectrum (CI), m/e 461 (M$^+$ + H).

2-Chloroethyl-trifluoromethylsulfonyl-amide (7a)

To a suspension of 2-chloroethyl amine hydrochloride (5.80 g; 0.05 mole) and powdered 3A molecular sieves (15g, from Linde Division, Union Carbide Corporation) in dichloro-ethane (100 mL) was added dropwise trifluoromethanesulfonyl chloride (5.3 mL; 0.025 mole) at room temperature under a nitrogen atmosphere. After the addition was completed, the mixture was stirred at 80°C for 20 hours. Filtration of the solid from reaction mixture, followed by evaporation of the filtrate gave 3.26g (31%) of crude liquid product. Vacuum distillation of the liquid gave pure 7a: IR (Neat) 3310, 3150, 1420, 1370, 1220, 1200 and 1150 cm^{-1}; mass spectrum (CI), m/e 212 (M$^+$ + H).

N,N'-Bis(2-chloroethyl)-N,N'-Bis(trifluoromethylsulfonyl) oxamide (7b)

Oxalyl chloride (0.58 ml; 0.0067 mole) was added drop-wise into a solution of 7a (2.80 g; 0.013 mole) and "Proton Sponge"^{R}(1.44 g; 0.0067 mole, from Aldrich Chemical Company, Inc) in methylene chloride (50 mL) at 0°C under a nitrogen atmos-phere. After the addition, the mixture was stirred at room temperature for 24 hours. Solvent was evaporated, and the residue was treated with diethyl ether. The ethereal solution

was dried over sodium sulfate. Evaporation of ether
followed by the treatment of residue with petroleum ether
gave 2.55 g (80%) of crude product. Recrystallization of
the crude product from petroleum ether afforded pure 7b:
IR (CH$_2$Cl$_2$) 1720, 1400, 1260, 1230, 1160 and 1120 cm^{-1};
mass spectrum (CI), m/e 477 (M$^+$ + H).

2-Chloro-3 pyridyl-trifluoromethylsulfonyl-amide (8a)

To a suspension of 2-chloro-3-aminopyridine (5.14 g;
0.04 mole) and powdered 3A molecular sieves (10 g) in
methylene chloride (60 mL) was added dropwise trifluoro
methanesulfonic anhydride (3.4 mL) at 0°C under a nitrogen
atmosphere. After the addition was completed, the mixture
was stirred at room temperature for 5 hours and then the
solid was filtered. Filtrate was evaporated and treated with
water to give 5.0 g (48%) of crude solid product. It was
collected and recrystallized from cyclohexane to give pure 8a:
IR(CH$_2$Cl$_2$) 3300, 1370, 1230, 1210 and 1140 cm^{-1}; NMR (CDCl$_3$)
δ 7.35 (m. 1H), 8.0 (2d, 1H, J=4Hz), 8.35 (2d, 1H, J=4Hz)
and 8.30 ppm (s 1NH); mass spectrum (EI), m/e 260 (M$^+$).

N,N'-Bis(2-chloro-3-pyridyl)-N,N'-Bis(trifluoromethyl sulfonyl) oxamide (8b)

Oxalyl chloride (0.53 mL; 0.006 mole) was added dropwise
into a stirring suspension of 8a (2.61 g; 0.01 mole) and
powdered 3A molecular sieves (5.0g) in methylene chloride
(75 mL) at 0°C under a nitrogen atmosphere. The mixture was
then heated to 60°C, held thereat for 3 hours, and then at
room temperature for 60 hours. The reaction mixture was

filtered and the filtrate was evaporated to dryness.
The resulting residue was extracted with diethyl ether,
and the combined ethereal extracts were dried over sodium
sulfate. Evaporation of the dried ethereal solution obtained
2.33 g (81%) of crude product. Recrystallization of the
crude product from cyclohexane gave the desired product 8b:
IR (CH$_2$Cl$_2$) 1750, 1730, 1420, 1260, 1220 and 1130 cm^{-1};
NMR (CDCl$_3$) δ7.50 (m 1H), 8.10 (2a, 1H, J=4H), and 8.5 ppm
(m 1H); mass spectrum (EI), m/e 574 (M$^+$).

Attempted Synthesis of 3,3'- [oxalyl bis [(trifluoromethyl) sulfonyl] imino]] bis (2-chloro-1-methylpyridinium trifluoro-methanesulfonate) (8c)

To a solution of 8b (0.5 g; 0.001 mole) in methylene
chloride (20 mL) was added methyl trifluoromethanesulfonate
(0.25 g; 0.0015 mole) at room temperature under a nitrogen
atmosphere. The mixture was stirred at room temperature for
20 hours. Evaporation of the reaction mixture gave a yellow
gummy material (0.9g). Its IR (neat) spectrum indicated the
oxalate C=O band at 1740 cm^{-1}. Attempts to obtain a pure
product have not been successful. Therefore it is not certain
whether 8c has actually been made. In another experiment
a solution of 8b (1 g) and methyl iodide (0.5 mL) in toluene
(20 mL) was heated at 80°C for 3 hours followed by stirring
the mixture at room temperature for another 60 hours. Evapor-
ation of the reaction mixture gave a residual solid, which
was indicated by its IR and NMR spectra to be unchanged 8b.

Bis(3-pyridyl)oxalate (9a)

To a solution of 3-hydroxy pyridine (4.76 g; 0.05 mole) and triethylamine (5.00 g, 0.05 mole) in 1,2-dimethoxyethane (100 mL) was added dropwise oxalyl chloride (2.2 mL; 0.025 mole) at room temperature under a nitrogen atmosphere. After the addition was completed, the mixture was stirred at room temperature for one hour, then heated to reflux for two hours. The reaction mixture was evaporated to dryness, and the residue was washed three times with chloroform (90 mL). The white solid that remained after chloroform treatment was separated by filtration (weight, 5.0g). IR spectrum (Nujal) indicated the expected carbonyl band of 9a at 1760 cm^{-1}.

3-Hydroxy-1-methyl pyridinium-trifluoromethanesulfonate oxalate Ester (9b)

To a solution of 9a (1g, 0.0004 mole) in methylene chloride (50 mL) was added dropwise methyl trifluoromethane sulfonate (1 mL) at 0°C. After the addition was completed, the mixture was stirred at 0°C for 1 hour, then at room temperature for another 4 hours. The white precipitate was seprated on a filter and then dried under vacuum to give the desired product 9b (1.92 g, 100%): IR (Najol) 3100, 1780, 1500, 1460, 1270, 1210, 1160 and 1100 cm^{-1}; NMR (DMSO-d$_6$) δ 4.3 (s, 6H), 7.95 (t, 2H, J=2 Hz) and 8.50 ppm (t, 2H, J=2Hz). This material was highly hygroscopic and attempts to obtain an analytically pure sample have thus far been unsuccessful.

1,1'-Oxalyl bis [(2-chloromethyl)benzimidazole] (10)

Oxalyl chloride (3.5 mL; 0.04 mole) was added drop-
wise into a stirring solution of 2-chloro-methylbenzimidazole
(10 g; 0.06 mole) in 1,2-di-methoxyethane (100 mL) at 0°C
under a nitrogen atmosphere. After the addition was completed,
pleted, the mixture was stirred at 0°C for an additional
hour. Solid was filtered, and the filtrate was evaporated
to dryness. The gummy brown material obtained from
evaporation was digested with anhydrous ether. Solid thus
formed was filtered immediately. Its IR spectrum (Nujol)
showed the characteristic C=O band at 1700 cm^{-1}. However,
the product appeared to be unstable, it decomposed slowly
upon standing at room temperature. Attempted recrystalli-
zation from organic solvents failed.

1,1'-oxalylbis [2-Methylbenzimidazole] (11a)

Oxaly chloride (2.5 mL. 0.025 mole) was added dropwise
into a solution of 2-methylbenzimidazole (5.28 g; 0.04 mole)
and triethylamine (4g; 0.04 mole) in dry tetrahydrofuron
(120 mL) at 0°C under a nitrogen atmosphere. After the
addition was completed, the mixture was stirred at 0°C for
one hour, and then at room temperature for another hour.
The solid precipitate was filtered. Evaporation of the
filtrate gave 5.82 g (91.5%) of crude product. Its IR
spectrum (Nujol) showed a strong C=O band at 1700 cm^{-1}.

1,1'-oxalyl bis(2,3-dimethylbenzimidazolium trifluoromethane sulfonate (11b)

To a solution of crude 11a (2.4g; 0.075 mole) in methylene chloride (80 mL) was added in portions methyl trifluoromethane sulfonate (2 mL) at 0°C. The mixture was then stirred at room temperature for 48 hours. A light green solid precipitate was filtered and dried (3.27g). Its IR spectrum (Nujol) showed bands due to C=O (1700 cm^{-1}), SO$_2$ (1160 and 1180 cm^{-1}) and CF$_3$ (1400 and 1380 cm^{-1}). The quaternary ammonium compound (11b) was found to be unstable on standing at room temperature although it was chemiluminescent in the organic solvent system, it was not chemiluminescent in aqueous media containing hydrogen peroxide.

6. __References__

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